

EXTENSION OF THE N_2^+ (C-X) BANDS IN THE FAR ULTRAVIOLET REGION[†]

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AN INVESTIGATION of the N_2^+ (C-X) bands was made using an 84-cm normal-incidence vacuum spectrograph. Two types of discharge tubes were used: one (II-shape) for an uncondensed and the other (straight type) for a condensed discharge. Not only were pure N_2 and pure NO gases used in both tubes, but also mixtures of a trace of these with a large amount of helium were fed into the tubes. In each case the gas was pumped continuously through the spectrograph, while the pressure inside the tube was several mm.

In the case of the uncondensed discharge of pure N_2 and pure NO, we could not obtain the N_2^+ (C-X) bands. However, in the condensed discharge of these pure gases, the bands appeared very weakly; furthermore, they appeared only in the range $v' < 3$. When we used mixtures of the gases with helium, the system of bands appeared quite strongly in both the condensed and uncondensed discharges. Only the bands due to the transitions between $v' \geq 3$ and various v'' were present, as was previously observed by Watson and Koontz¹ in the condensed discharge of ($N_2 + He$). In these cases, we can make an extension of the system below about $1,300\text{\AA}$. The results are shown in Table I, compared with the values of Watson and Koontz.

Setlow², from a consideration of the intensity distribution, had proposed an alternative v' -assignment, and his suggestion has recently been confirmed by Miescher and Baer³ from measurements of the isotope shifts due to $(N_2^{15})^+$, $(N^{15}N^{14})^+$, and $(N_2^{14})^+$ ionized molecules. Thus the corrected v' -assignment has been adopted in Table I.

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¹W. W. Watson and P. G. Koontz, Phys. Rev. **46**, 32 (1934).

²R. B. Setlow, Phys. Rev. **74**, 153 (1948).

³R. Miescher and P. Baer, Nature, Lond. **169**, 581 (1952).

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TABLE I

$C^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ BANDS OF N_2^+

v'	v''	ν observed (cm^{-1}) present	I	ν (cm^{-1}) Watson and Koontz	I
3	11	48551.7	3	48553.7	4
4	12	48727.7	2	48729.5	3
5	13	48907.8	1	48912.5	2
6	14	49089.9	0	49097.6	1
7	15	49280.3*	0		
11	8	50127.8*	0	50134.6	0
22	9	50248.7*	0	50257.6	1
33	10	50387.2	7	50391.5	10
44	11	50526.4	6	50530.6	8
55	12	50672.0	3	50675.7	6
66	13	50821.7	3	50824.2	4
77	14	50965.3	1	50975.2	1
88	15	51126.6	0	51127.0	1
99	16			51285.2	0
100	17			51426.8	0
110	6	51991.5*	0	51996.4	1
121	7	52063.5*	0	52073.1	2
222	8	52154.5*	0	52160.5	2
333	9	52259.6	6	52261.7	9
444	10	52366.4	5	52363.1	7
555	11	52474.6	4	52472.6	5
666	12	52586.9	3	52585.3	3
777	13	52700.5	0	52695.0	0
888	14	52810.3*	0	52809.1	0
999	5	53997.7*	0	54006.1	2d
111	6	54040.3*	0	54046.9	2
222	7	54095.0*	0	54100.2	1
333	8	54166.1	6	54165.3	6
444	9	54234.8	3	54233.4	3
555	10	54306.5	0	54308.6	1
666	5				
777	4	56042.8*	1	56050.4	1d
888	3			56074.0	1
999	2	56134.0	0	56138.7	1
111	1	56178.5	0	56180.6	1
222	0	56216.7	0	56224.2	0
333	6				
444	5	58079.9	6	58078.9	3d
555	4	60082.0	3		
666	3	62057.7	5		
777	2	62130.3	4		
888	1	64137.5	5		
999	0	64201.9	5		
111	3	66173.9	2		
222	2	66322.8	2		
333	1	68290.6	3		
444	0	68454.6	3		
555	0	70640.9	3		
666	0	72600.6	2		

* observed in the disruptive discharges of pure nitrogen and pure nitric oxide.

As we mentioned above, in the case of the mixture of gases ($N_2 + He$, $NO + He$), we could not observe the bands due to the transitions ($v' < 3$) $\rightarrow v''$, and in each sequence the bands ($v' = 3$) $\rightarrow v''$ were the strongest. This feature, which had already

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been observed by Watson and Koontz, was attributed by them to the resonance excitation of the $v' = 3$ level by He^+ . If we take Gaydon's value⁴ of the dissociation energy of N_2 , (9.764eV), then the energy of the $v' = 3$ level of the C-state, (24.330eV), is nearly equal to the dissociation limit ($N^4S + N^+3P$), (24.304eV), of the N_2^+ ground state. Douglas⁵ recently proposed the possibility of inverse predissociation at $v' = 3$ to explain an anomalously high population at the level. If we consider the resonance excitation by He^+ , (24.580eV), the population might be rather high in the $v' = 4$ level, (24.576eV), instead of $v' = 3$, (24.330eV). Whenever this system is well developed, the line spectra of atomic nitrogen appear very strongly, and we can also observe an irregularity in the ΔG curve of the upper C-state between $v' = 2$ and $v' = 3$. These observations seem to support the theory of inverse predissociation at the $v' = 3$ level.

Takamine and his co-workers⁶ have observed a change in the intensity distribution of the band system when neon was used in place of helium in the mixture. They attributed the distribution obtained with neon to a high population in the $v' = 0$ and $v' = 1$ levels due to three body collisions; $Ne^+ + N_2 + N(^2D) \rightarrow Ne + N_2^+ + N(^4S)$. Their suggestion seems probable but, if the resonance excitation is the major factor, then the (1,6) and (2,7) bands should be stronger than the (0,5) band in the $\Delta V = -5$ sequence. This follows from the fact that the $v' = 1,2$ levels are closer to 23.934eV, which is the sum of the ionization potentials of Ne and the excitation energy of $N(^2D)$.

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⁴A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules (Dover Publications, Inc: New York, 1950).

⁵A. E. Douglas, Canad. J. Phys. **30**, 302 (1952)

⁶T. Takamine, T. Suga, and Y. Tanaka, Sci. Pap. Inst. Phys. Chem. Res., Tokyo **36**, 437 (1939).